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OXIDATION STATES AND FERMI-LEVEL PINNING ON GaAs(1 1 0) SURFACE

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Fermi-level pinning produced by oxygen adsorption on the GaAs(1 1 0) cleavage surface both at 300 (in chamber) and 77 K (in liquid N_2) has been studied using the polarization modulated reflectivity technique. Specific transformations of spectra of doped samples have allowed to follow the kinetics of barrier formation. It has been found that the creation of acceptor and donor pinning levels on the surface correlates with two essentially different oxidation states. The first one is the chemisorption of atomic oxygen. We suggest that it forms patches on the surface. The second phase is supposed to be a surface oxide.

ALTHOUGH THE INTERACTION of oxygen with the GaAs(1 1 0) clean cleavage surface has been extensively studied [1–23], no microscopic model of oxidation process is generally accepted nowadays. The major controversy concerns the degree of homogeneity of the surface oxide layer and the onset of subsurface oxidation at room temperature [11–18].

A more clear understanding has been achieved of oxidation at lower temperatures [12, 19–21]. In [19, 20], the physisorption of molecular oxygen has been evidenced at 45 K which converts to a chemisorption state at about 60 K. The latter state is the only one observed in the temperature interval from about 60 to 170 K ("intermediate" state [20]). After [12, 13] we label it T_1.

At higher temperatures, including 300 K, the T_1-state was observed also but for low coverages only [12]. Starting at about 10^6 L of exposures to molecular oxygen, dramatic changes in the oxidation state have been shown by a variety of different techniques [7–23]. The new state appearing at these exposures was labelled T_2 in [12, 13]. Just this state is a matter of controversy mentioned above [16–18].

Another important phenomenon which may be observed in the course of oxidation is the bending of electronic bands near the surface due to the creation of surface levels within the energy gap of GaAs which pin the Fermi level [1–6]. It was established that in *n*-type crystals the band bending is determined by acceptor type levels with the energy position of $E_v + 0.75\,\text{eV}$ [2, 3] (E_v is the valence band maximum). In *p*-type samples the pinning levels are of donor type at $E_v + 0.5\,\text{eV}$ [2, 3]. It is generally believed that both types of the levels appear simultaneously in the course of adsorption of foreign atoms [24]. In the present paper we show that this is not the case at least for oxidation. Our results evidence that the T_1-type oxidation produces the acceptors only, and the T_2 state correlates with creation of the donors.

The (1 1 0) surfaces of GaAs were prepared by cleavage either in liquid nitrogen (77 K) or at room temperature in ultrahigh vacuum chamber with the base pressure of about 10^{-8} Pa. In the first case oxidation of the surfaces occured immediately in liquid N_2, and in the chamber it was done using an O_2-source.

Our study was performed with the use of polarization modulated reflectivity (PMR) technique [26–29]. The linear polarization of incident light was modulated between the $[\bar{1}\,1\,0]$ and $[0\,0\,1]$ directions lying in the (1 1 0) crystal face. The measured quantity was

$$\frac{\Delta R}{R} = \frac{R_\parallel - R_\perp}{R_\parallel},$$

where $R_\parallel$ and $R_\perp$ are the reflectances for light polarized along the $[\bar{1}\,1\,0]$ and $[0\,0\,1]$ directions, respectively. The spectral variation of $\Delta R/R$ was recorded.

The polarization spectra were found to exhibit a structure due to the optical transitions which involve intrinsic surface states, and some features in the region of the well-known E_1 and $E_1 + \Delta_1$ bulk transitions [26–28]. Since GaAs has cubic symmetry, the display of the bulk transitions in the PMR spectra may be allowed by symmetry breaking perturbations only. Among them is the near-surface electric field which is present in the case of band bending [28]. The field influences optical properties via the Franz–Keldysh effect [28, 30, 31]. Symmetry considerations show that this effect should have a polarization dependence, and hence the optical reflectance should be somewhat different for the light polarized along the $[\bar{1}\,1\,0]$ and $[0\,0\,1]$

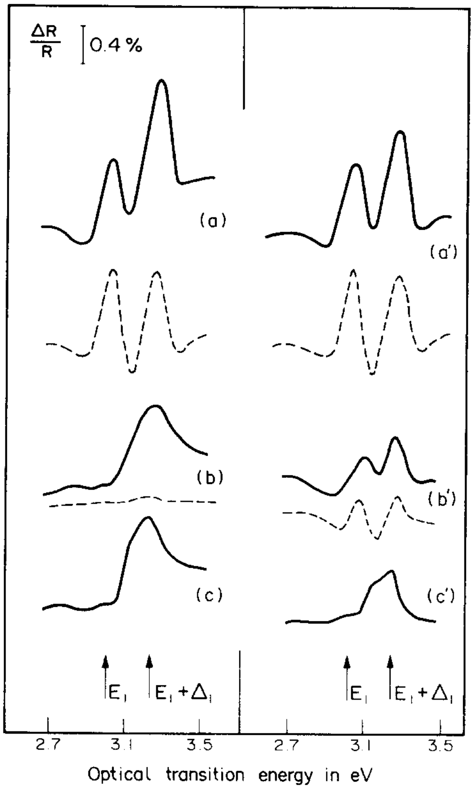

Fig. 1. PMR spectra of the (1 1 0) surfaces of GaAs cleaved in liquid N_2 — curves *a*, *b* and *c*, and after oxidation in air — curves *a'*, *b'* and *c'*, in case of doped *n*-type (*a*), *p*-type (*b*) and lightly doped (*c*) samples. The dashed curves show the field related signals.

directions. This gives rise to a nonzero PMR signal, $\Delta R/R$.

In order the surface field to be strong enough ($\simeq 10^5\,\mathrm{V\,cm^{-1}}$) we used doped GaAs samples of carrier concentration of about $2 \times 10^{18}\,\mathrm{cm^{-3}}$, both of *n*- and *p*-types. For comparison, we also studied lightly doped samples with $n \simeq 10^{16}\,\mathrm{cm^{-3}}$ whose reflection spectra exhibited no field induced features.

Spectra of the (1 1 0) surfaces prepared by cleavage in liquid N_2 differed significantly from those of the atomically clean faces reported in [26, 27]. Due to a rapid oxidation the structure associated with dangling bonds, and typical for the clean surfaces, was suppressed. Moreover, contrary to the case of clean faces, the PMR spectra of the cleaved-in-N_2 samples appeared to be strongly dependent on the type and level of doping. Fig. 1 shows the PMR curves taken on doped *n*-type (curve *a*), *p*-type (curve *b*) and lightly doped (curve *c*) samples cleaved and held in N_2 for 2 h.

The PMR spectra in the region of the E_1 and $E_1 + \Delta_1$ bulk transitions shown in Fig. 1 may be treated as a sum of two signals [28]. One of the contributions is induced by the surface field, E_s. It is specific of the doped crystals. The other contribution which does not depend on E_s and is always present in the spectra, is supposed to be due to a deformation of a surface layer. It is represented by the spectrum of the undoped sample — see Fig. 1(c). Hence the differences between the spectra of doped and undoped samples should provide the contributions of the field dependent response — they are presented by the dashed curves. A pronounced signal of this type is seen for *n*-type crystals (*a*).

As the doping of *n*- and *p*-type crystals was practically the same, one would expect analogous spectra to be shown by the *p*-type samples in case the surface field had a value close to that in the *n*-type. However, the spectrum of the *p*-type — see Fig. 1(b), is identical to that of the lightly doped sample, *c*, without any field contribution.

Such a different behaviour of *n*- and *p*-type crystals indicates that the oxidation in liquid N_2 induces the acceptor surface levels only which pin the Fermi level in *n*-type samples. No field related signal and hence no Fermi-level pinning by donor levels were observed on *p*-GaAs after 6 h of exposure in liquid N_2.

The cleaved-in-N_2 samples were then exposed to air for 12 h at room temperature and reimmersed into nitrogen. This procedure should lead to a heavy oxidation of the surfaces. In case of *n*-type and lightly doped samples, it produces some attenuation of the structure not related to the electric field. As dashed curve *a'* shows, the electric field contribution in case of *n*-type stays the same as before (*a*). On the contrary, the spectrum of the *p*-type crystal, *b'*, shows a significant change providing evidence of the appearance of the field (see the dashed curve).

These data unambiguously show that the creation of the acceptor and donor surface levels requires essentially different states of oxidation. Formation of the acceptor pinning levels should be related to the T_1 oxidation state, the only possible one at 77 K [12, 20]. The birth of the donor levels may be correlated with the T_2 state which is the main phase at room temperature [12, 13]. This conclusion is confirmed by our studies of oxidation in the vacuum chamber at room temperature.

Room temperature PMR spectra of GaAs(1 1 0) surfaces are shown in Fig. 2. Curve a corresponds to a clean surface. It is essentially the same for doped *n*- and *p*-type and lightly doped crystals that evidences that there is no band bending near the clean cleavage surface of GaAs. The S_{1-3} features are due to the dangling bond states.

With oxidation all of the samples show suppression of the S_{1-3} features. The rate of the quenching of peaks S_{1-3} was used to estimate the relative area, θ, of

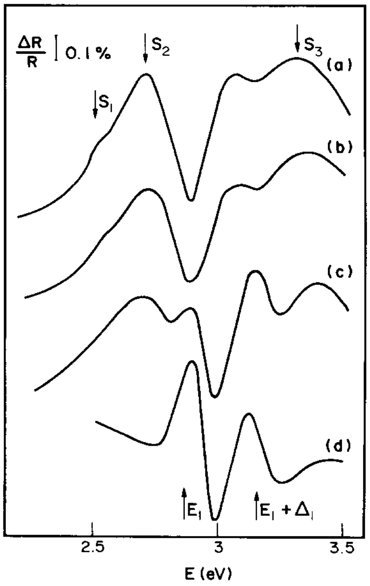

Fig. 2. PMR spectra of GaAs (1 1 0) surface at room temperature: *a* — atomically clean surface, *b* — partly oxidated ($\theta \simeq 0.1$) *p*-type, *c* — the same for *n*-type, and *d* — the difference between spectra *c* and *b*.

the surface "spoiled" by the oxygen adsorption [32]. It is plausible that the adsorption of an oxygen molecule produces a reconstruction of a large number of atomic bonds within some area around the molecule (long-range effects were discussed also in [33]). If independent adsorption of oxygen molecules were assumed in this case, then the long-range rearrangement of the surface layer would cause an essential broadening of the S_{1-3} peaks. However, this structure disappears practically without any broadening. This fact evidences that the adsorbed oxygen forms patches. This conclusion is true also for low-temperature oxidation which has been performed in vapours above the level of liquid He.

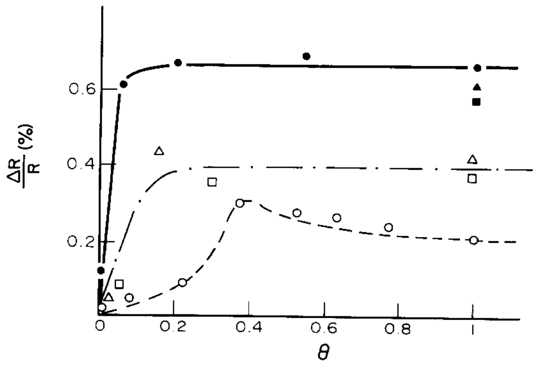

Fig. 3. Dependence of the field signal on θ in case of *n*- (filled symbols) and *p*-type (open symbols) GaAs. Circles correspond to adsorption of oxygen. For comparison, are given the results for Cs (triangles) and Sb (squares) adsorption.

Curves *b* and *c* in Fig. 2 show the PMR spectra of doped *p*- and *n*-type crystals, respectively, recorded after oxidation corresponding to $\theta \simeq 0.1$. The spectrum of the undoped crystal is not shown here because it is practically the same, at the same θ, as spectrum *b*. On the contrary, the difference between the spectra of the *n*-type and the undoped (or the *p*-type) crystals is quite obvious. It is given by curve *d* which is due to the field contribution in the *n*-type sample.

The difference between spectra of doped and undoped samples taken for the same θ were used to plot the dependences of the amplitudes of the field induced signals on the θ-value — see Fig. 3. In case of *n*-GaAs the field-related contribution saturates at $\theta < 0.1$ that is in accord with previous studies [1–6] (filled circles).

For *p*-GaAs, we obtain a more complicated kinetics of the barrier formation. Here two anomalies are evident (open circles): (i) the kinetics is essentially slower than that in the case of *n*-type, that is clearly seen already from Fig. 2, and (ii) at heavy oxidation the band bending decreases by almost two times. The slow pinning for *p*-type crystals agrees nicely with the experimental data of Spicer *et al.* [2, 3, 34]. The exposures required for the Fermi-level pinning in their case are of the order of 10^6 L and more. They are typical of the formation of the T_2 oxidation state [7–23].

The observed difference between the *n*- and *p*-type kinetics indicate the selective creation of the pinning acceptors and donors. Again as for 77 K, we may suggest that the T_1 oxidation (small θ) produces the acceptors only, and the T_2 oxidation (larger θ) creates the donors. The decrease of the band bending in *p*-type GaAs at $\theta > 0.4$ may be associated with the formation of a thick layer in presence of excited oxygen in our chamber.

Figure 2 shows also kinetics of the Schottky-barrier formation at submonolayer coverages of Cs (triangles) and Sb (squares) on *n*- and *p*-type GaAs(1 1 0) cleavage surfaces measured by the PMR technique. No marked deviations from the literature data and the unified defect model [2, 10] have been observed in this case.

Concluding, we have shown that two different mechanisms are to be responsible for creation of the acceptor and donor pinning levels on the oxidized GaAs(1 1 0) surface. Creation of acceptors correlates with the chemisorption of oxygen, or the T_1 state, and hence may be understood within the framework of the unified defect model [2, 10]. However, as for the donors, the situation is more complicated. The donor levels are produced by T_2-type oxidation which may include some form of subsurface oxidation [13–15, 18].

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